nitrate is coordinated to platinum; for example, Pt–O$_{av}$ = 2.01 Å in *cis*-$Pt(NH_3)_2(NO_3)_2$.[11] A similar increase in the axial Pt–N distance is revealed when the average Pt–NO_2 value of 2.18 (1) Å in compound **3** is compared to Pt–N distances of ~2.02 Å found in mononuclear platinum nitrite complexes.[12] A comparable increase in metal-to-axial-ligand distance is also observed in the dirhodium(II) tetracarboxylate complexes.

The structures of **2** and **3** compare favorably with that of $[(4\text{-}CH_3C_5H_4N)(CH_3)_2Pt(O_2CCF_3)_2Pt(CH_3)_2(4\text{-}CH_3C_5H_4N)]$,[4] which has a Pt–Pt distance of 2.557 (1) Å and canted, twisted Me_2Pt units analogous to the $(NH_3)_2Pt$ units in a variety of *cis*-diammineplatinum complexes.[7] A family of platinum(III) dimers that lacks such sterically interacting ligands includes $K_2[Pt_2(SO_4)_4(H_2O)_2]$,[5] $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$,[13] and $K_2[Pt_2(SO_4)_4(OSMe_2)_2]\cdot 4H_2O$,[13] which have metal–metal bond lengths of 2.466, 2.486 (2), and 2.471 (1) Å, respectively. The shorter metal–metal distances observed for these molecules may be due to the absence of unfavorable nonbonded interactions between parallel platinum coordination planes. Finally, the Pt–Pt distance of 2.575 (1) Å observed for the nitro complex **3** may be compared with the value of 2.584 (1) Å reported for the deprotonated 1-methylcytosine dimer, $[(NO_2)(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2(NO_2)]^{n+}$ (**4**), where *n* was assigned as 1.[14] The near equality of the metal–metal distances in **3** and **4** further underscores the need to reinvestigate the assignment of the Pt(2.5) oxidation state in the deprotonated 1-methylcytosine dimer to determine whether **4** might really be a binuclear Pt(III) complex, a possibility suggested previously.[7] The synthetic route to Pt(III) dimers described here should provide a convenient way to make compound **4**, the preparation of which has been difficult to reproduce.[14]

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Registry No. **2**, 81277-22-7; **3**, 81277-25-0.

Supplementary Material Available: Atomic positional and thermal parameters for compounds 2 and 3 (3 pages). Ordering information is given on any current masthead page.

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(12) (a) Kaduk, J. A.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3278. (b) Boer, F. P.; Carter, V. B.; Turley, J. W. *Ibid.* **1971**, *10*, 651.
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Hydridic Reduction of Carbon Monoxide on Various Iron Dimers

Sir:

We have previously reported the reduction of carbon monoxide on $Cp_2Fe_2(CO)_4$ by reaction with $LiAlH_4$ (LAH).[1,2]

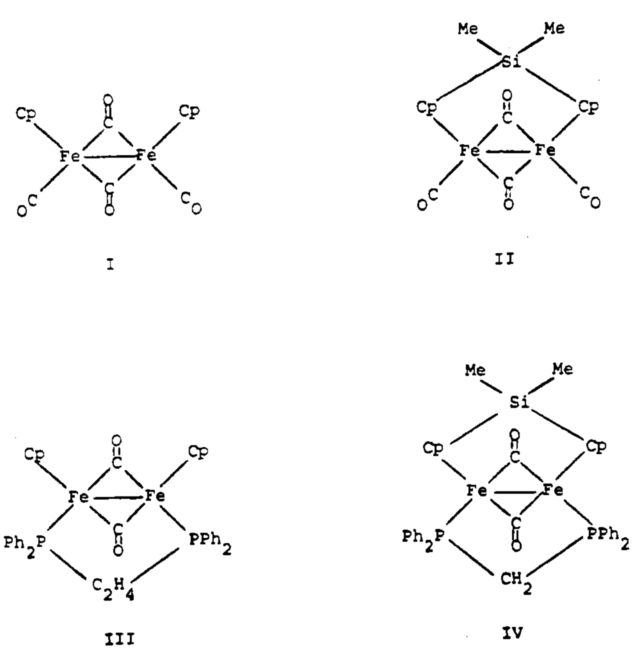

Figure 1. Structures of the iron dimers that have been reacted with LAH.

The products were hydrocarbons ranging up to butane and butene.[1,2] The specific role of the terminal and bridging carbonyls could not be assessed in these studies. The recent preparation of the new iron dimers shown in Figure 1 has allowed a determination of the necessity of terminal CO's for reduction chemistry.[3]

Experimental Section. Purification of solvents was effected as previously described.[2] The iron dimers were prepared, purified, and characterized as reported earlier.[3] $Cp_2Fe_2(CO)_4$ (Strem Chemical) and LAH (Alfa) were used as received.

The reduction reactions were accomplished as described previously with 0.25 mmol of iron dimer and 5.0 mmol of LAH in toluene for a specified period of time. Gas chromatographic analysis was performed as in the earlier work.[2] After the reduction was completed, the solution was filtered and the infrared spectrum was recorded.

Results and Discussion. Reaction of $Me_2Si[(\eta^5\text{-}C_5H_4)Fe(Co)_2]_2$ with LAH produced hydrocarbon products very similar to those observed in reduction of CO on $Cp_2Fe_2(CO)_4$,[1,2] and these results are summarized in Tables I and II. The amounts of olefins declined during the course of the reaction just as observed for reduction on $Cp_2Fe_2(CO)_4$. The linking of the cyclopentadienes evidently has very little effect on the CO reduction chemistery. No Me_2SiH_2 was detected by GC analysis, suggesting that the bridging is not disrupted by LAH.

Reactions of $C_2H_4[(Ph)_2PFeCp(CO)]_2$ (III) and $Me_2Si[(\eta^5\text{-}C_5H_4)Fe(CO)]_2L$ (L = bridging $Ph_2PCH_2PPh_2$) (IV) with LAH show essentially no hydrocarbon products. The amounts are 2 orders of magnitude less than seen in reactions of I and II. The amounts of hydrocarbons do not increase with time, and the dimers are recovered after reaction times of 10 days. Apparently, trace impurities are giving rise to the hydrocarbon production and complexes III and IV do not react with LAH.[4] The reactions of these two complexes with LAH are very different from the reaction with $Cp_2Fe_2(CO)_4$.

The feature of primary importance appears to be the presence or absence of terminal carbonyls. Compounds I and

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(1) Wong, A.; Atwood, J. D. *J. Organomet. Chem.* **1980**, *199*, C90.
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(3) Nelson, G. O.; Wright, M. E. *J. Organomet. Chem.* **1981**, *206*, C21 and references therein.
(4) It is very difficult to remove trace quantities of tetranuclear complexes with the bidentate phosphines bridging two iron dimers.

0020-1669/82/1321-2117$01.25/0

Table I. Hydrocarbon Products of the Reduction of Carbon Monoxide on $Cp_2Fe_2(CO)_4$[a]

time	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}
3 h	3.0×10^{-2}	6.0×10^{-2}	4.0×10^{-2}	1.7×10^{-2}	2.1×10^{-2}	trace	trace
1 day	0.12		0.26		0.10		trace
14 days	0.61		0.69		0.22		2.6×10^{-2}

[a] mmol of hydrocarbon product/mmol of iron complex.

Table II. Hydrocarbon Products Formed in the Reduction of Carbon Monoxide on $Me_2Si[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$[a]

time	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
$1^1/_2$ h	2.6×10^{-2}	4.2×10^{-2}	4.1×10^{-2}	0.9×10^{-2}	1.0×10^{-2}
2 days	0.22		0.17		2.6×10^{-2}
10 days	1.12		0.63		0.22

[a] mmol of hydrocarbon/mmol of iron complex.

Table III. Hydrocarbon Products Formed by Reaction of LAH with $Co_2(CO)_8$ and $Co_2(CO)_6(PPh_3)_2$[a]

	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
$Co_2(CO)_8$	0.41	0.04	0.37	0.002	0.003
$Co_2(CO)_6(PPh_3)_2$	0.40		0.24		0.08

[a] The reactions were studied with a 20-fold excess of LAH for 1 week. The amounts are given in mmol of hydrocarbon/mmol of cobalt complex.

II, which have terminal CO's, undergo carbon monoxide reduction reactions, forming very similar products. Complexes III and IV, which have only bridging CO's, do not undergo CO reduction chemistry when treated with LAH. The presumed first step in the reduction process, H^- addition to coordinated carbon monoxide, must not occur for the bridging carbonyls, which have a higher electron density.[5] It has been previously noted that nucleophilic attack on coordinated carbon monoxide depends on the electron density at the CO.[6,7] The presence of the phosphine donor ligand will change the electron density at the metal, but we do not believe that the change is sufficient to significantly affect the reactivity toward LAH. Comparison of the reactions of LAH with $Co_2(CO)_8$ and $Co_2(CO)_6(PPh_3)_2$ shows little inhibition of CO reduction chemistry on substitution of a phosphine for CO. The data are shown in Table III. The agreement in quantities of hydrocarbons for $Co_2(CO)_8$ and $Co_2(CO)_6(PPh_3)_2$ indicates that the replacement of CO by PPh_3 does not cause marked changes in the reaction and not caused that the difference in reactivity between compounds I and II compared to that of III and IV is due to the presence or absence of terminal CO's and is not caused by electronic differences.

The data reported herein provide evidence for the necessity of terminal carbon monoxide for reduction to hydrocarbons by LAH. This result is understandable in terms of an initial step of hydride attack on the terminal CO for reduction chemistry which will be further explored.

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Registry No. I, 12154-95-9; II, 42830-83-1; $Co_2(CO)_8$, 10210-68-1; $Co_2(CO)_6(PPh_3)_2$, 24212-54-2.

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Additions and Corrections

1980, Volume 19

W. C. Trogler: Symmetry Aspects of the Electronic Spectra of Binuclear Complexes with D_{3h} Symmetry.

Page 698. The expression [4] represents a symmetric orbital function and can be assigned a singlet spin wave function; however, the transition to this state is dipole forbidden and should occur at higher energy. These types of excitations were not considered in the assignment of the dipole-allowed transitions of $M_2X_9^{n-}$ complexes but would be relevant if one were interested in forbidden transitions to higher energy of the allowed metal-localized absorption bands.—W. C. Trogler

1981, Volume 20

Andrew Fuller Kirby and Richard Alan Palmer*: Single-Crystal Electronic Absorption of Tris(1,3-diphenyl-1,3-propanedionato)aquoneodymium(III): Oscillator Strength of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ Hypersensitive Transition.

Page 1031. In Table I the positional parameter x for C(1) should read 0.1337 (21) instead of 0.1137 (21).—Richard A. Palmer

1982, Volume 21

Michael H. Dickman and Robert J. Doedens*: Structure of Chloro(2,2,6,6-tetramethylpiperidinyl-1-oxo-*O,N*)(triphenylphosphine)palladium(II), a Metal Complex of a Reduced Nitroxyl Radical.

Pages 682, 683. The title compound is referred to by two different systematic names in this paper. The correct name is that given above.—Robert J. Doedens